Grundlagen der Chemie für Studierende des Maschinenbaus, Prof. Dr. Meier

Chemistry for Students of Mechanical Engineering

Friday, 22nd February 2013, 15:00-18:00

No unauthorised resources (*e.g.* lecture notes, textbooks etc.) may be used during the examination. Any attempt to use such unauthorised resources will be considered as cheating, and will lead to immediate exclusion from the examination and a mark of 5,0.

Foreign students may use a dictionary (mother tongue – English) but this may not contain any handwritten notes. The use of a calculator is not permitted.

Numerical answers that are given without showing any working or explanation will receive no marks.

In general, short answers with keywords will be sufficient; long essays are not necessary! To illustrate or explain a point, a clear sketch is often sufficient!

The maximum number of points for each question is given in parentheses.

0-49,5	50-54	55-59	60-64	65-70	71-75	76-80	81-85	86-90	91-95	96-100
5,0	4,0	3,7	3,3	3,0	2,7	2,3	2,0	1,7	1,3	1,0

Question 1:

a) What is the significance of the two numbers in the nuclide $^{37}_{20}\mathrm{Cl}$? (1P)

$^{\text{Protonen + Neutronen} \rightarrow 37}_{\text{Protonenzahl} \rightarrow 20}\mathrm{Cl}$ **:** ***The nucleus contains 20 protons and (37 – 20) = 17 neutrons.***

b) What is observed when the light emitted by an energetically-excited atom is passed through a prism and separated into its constituent wavelengths?

A series of sharp emission lines, at wavelengths characteristic for atoms of that element, is seen. (1P)

Why was this observation important for the understanding of atomic structure?

That the electrons in an atom can only adopt certain (quantised) energies (1P)

c) Give the electron configuration of the element zirconium (Zr). (1P)

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$

d) How do the radii of atoms change on going from left to right across a Row in the Periodic Table, and how do they change on going down a Group? Give reasons for your answers. (3P)

Across a Period: radius decreases (outermost electrons attracted more strongly by the nucleus due to increasing number of protons in nucleus).
Down a Group: radius increases (number of shells increasing).

e) Use the VSEPR model to give the three-dimensional structures of the $BeCl_2$, BF_3, $SiCl_4$ und NH_3 molecules (4P)

$BeCl_2$: linear **BF_3: trigonal planar**
$SiCl_4$: tetrahedral **NH_3: trigonal pyramid**
A clear sketch is also OK.

f) Which of the molecules in question e) have a dipole moment? (4P)

$BeCl_2$: **no** BF_3: **no** $SiCl_4$: **no** NH_3: **yes**

g) What is understood by permanent dipoles and induced dipoles? (2P)

Permanent dipole: a polar covalent bond between two atoms of different electronegativity, with resultant opposite partial charges on the two atoms.
Induced dipole: a short-lived (transient) polarisation of a non-polar atom or molecule due to fluctuations in its local electron density

h) What are the characteristics of the structures of crystals? (1P)

A three-dimensional lattice with long-range order

i) Which simple rule tells us that elements of Group 6 tend to form dianions X^{2-}? (1P)

Inert gas rule (8 electron rule): the attempt by an atom to attain a stable inert gas electron configuration.

j) How does an osmotic pressure arise? (1P)

By the diffusion of solvent molecules through a semi-permeable membrane separating two solutions of different concentrations, from the less concentrated to the more concentrated, leading towards a partial equalisation of the concentrations. The liquid level on the more concentrated side becomes higher, resulting in the osmotic pressure.
(A sketch can be helpful here!)

k) Give two important properties of metals. (2P)

- **the valence electrons form a „free electron gas“ between positively charged ions**
- **electrical conductance**
- **thermal conductance**
- **ductility**
- **atoms form a crystalline lattice**

(any two of these!)

Question 2:

(a) What does Hess's Law tell us? (1P)

The enthalpy change for a reaction ΔH^o does not depend on the mechanism followed, but only on the starting and end points

(b) Give the equations that are used to calculate the changes in enthalpy, entropy and free energy for a reaction. (3P)

$$\Delta H = \sum \nu_i \cdot \Delta H_f^0 \text{ (products)} - \sum \nu_i \cdot \Delta H_f^0 \text{ (starting materials)}$$
$$\Delta S = \sum \nu_i \cdot \Delta S_f^0 \text{ (products)} - \sum \nu_i \cdot \Delta S_f^0 \text{ (starting materials)}$$

$$\Delta G = \sum \nu_i \cdot \Delta G_f^0 \text{ (products)} - \sum \nu_i \cdot \Delta G_f^0 \text{ (starting materials)}$$
$$\text{or } \Delta G = \Delta_R H - T \cdot \Delta_R S$$

(where ν_i is the stoichiometric coefficient of substance i in the reaction equation)

(c) A mixture of CO and H_2 ("Water Gas" or "Synthesis Gas") is formed when water vapour reacts with glowing coke (C). Give the equation for this reaction.

$C + H_2O \rightarrow CO + H_2$ (1P)

Calculate the changes in enthalpy ($\Delta H°$), in entropy ($\Delta S°$) and in free energy ($\Delta G°$) for the reaction, using the following values:

$\Delta H^o_f(CO) = -111$ kJ mol^{-1}, $^{\Delta}H^o_f(H_2O) = -241.8$ kJ mol^{-1}
$S^o(CO) = 198$ J mol^{-1} K^{-1}, $S^o(H_2O) = 188.8$ J mol^{-1} K^{-1},
$S^o(H_2) = 130.7$ J mol^{-1} K^{-1}, $S^o(C) = 5.7$ J mol^{-1} K^{-1}

$\Delta H = -111$ kJ mol^{-1} + 0 - (- 241.8 kJ mol^{-1}) - 0 = +130,8 kJ mol^{-1}
$\Delta S = 198$ J mol^{-1} K^{-1} + 130.7 J mol^{-1} K^{-1} – 188.8 J mol^{-1} K^{-1} – 5.7 J mol^{-1} K^{-1} = +134.2 J mol^{-1} K^{-1}
$\Delta G = [+130800 – (298\times134.2)]$ J mol^{-1} = +90808.4 J mol^{-1} = 90.8 kJ mol^{-1}
(3P)

(d) How is the change in Free Energy ($\Delta G°$) the criterion for whether a reaction takes place spontaneously?

A chemical reaction takes place spontaneously, when $\Delta G^o < 0$. (1P)

Use this criterion to explain why the formation of ethene from ethane (with elimination of H_2) is spontaneous at high temperatures, even though the reaction is endothermic

$\Delta G = \Delta H – T\Delta S$.
$\Delta S > 0$, because the reaction involves the formation of two gas molecules (C_2H_4 and H_2) from one (C_2H_6).
So at high enough T, $|T\Delta S| > |\Delta H|$, and $\Delta G < 0$. (1P)

(e) The formation of ammonia (NH_3) from its elements is an equilibrium reaction. Give the equation for the reaction, and explain why entropy decreases when the reaction takes place.

$N_2 + 3\ H_2 \leftrightarrows 2\ NH_3$

Entropy descreases because the number of gas molecules reduces from 4 to 2 as the reaction proceeds, reducing the disorder of the system and so the entropy. (2P)

In which direction does the equilibrium position shift, when:

- the temperature is (i) increased or (ii) decreased
- the pressure is (i) increased or (ii) decreased?

Explain your answers. (the reaction is exothermic: $\Delta H_f°(NH_3) = -46$ kJ mol^{-1})

- ***increase in T:*** **to the left (towards starting materials)** (½P)
- ***decrease in T:*** **to the right (towards product)** (½P)
- ***increase in P:*** **to the right (towards product)** (½P)
- ***decrease in P:*** **to the left (towards starting materials)** (½P)

Applying Le Chatelier's Principle: (1P)
On increasing T, the reaction shifts in the endothermic direction; on decreasing T in the exothermic direction. On increasing P the equilibrium shifts towards the side with fewer gas molecules; on decreasing P towards the side with more gas molecules (1P)

(f) For a reaction aA + bB ⇆ cC + dD, give the equation that relates the equilibrium constant K to the concentrations of the substances involved, and also the equation that relates K to a thermodynamic quantity.

$$\mathbf{K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}}$$ (½P)

$$\mathbf{\Delta G = -\,RT\,\ln K \quad or \quad K = \exp(-\Delta G/RT)}$$ (½P)

(g) At room temperature, the solubility product of CaF_2 is 4×10^{-12} $mol^3\ l^{-3}$. What is the concentration of Ca^{2+} in a saturated solution of CaF_2 in pure water, and what is $[Ca^{2+}]$ in a saturated solution of CaF_2 in water in which the concentration of F^- is 0.1 mol l^{-1}?

$[Ca^{2+}][F^-]^2 = 4\times10^{-12}\ (mol\ l^{-1})^3$

In pure water: $[F^-] = 2[Ca^{2+}]$
$[Ca^{2+}] \times 4[Ca^{2+}]^2 = 4[Ca^{2+}]^3 = 4\times10^{-12}\ (mol\ l^{-1})^3$
$[Pb^{2+}] = (1\times10^{-12})^{1/3}\ mol\ l^{-1} = 1\times10^{-4}\ mol\ l^{-1}$

$[F^-] = 0.1\ mol^{-1} \rightarrow [Ca^{2+}] \times (0.1)^2 = 4\times10^{-12}\ (mol\ l^{-1})^3$
$[Ca^{2+}] = 4\times10^{-10}\ mol\ l^{-1}$ (2P)

(h) What is understood by (i) the rate, and (ii) the order of a chemical reaction?

***Rate of reaction*: rate of change of the concentration of a substance involved in the reaction with time**
***Reaction order*: *e.g.* if the rate = $k[A]^m[B]^n$, then the reaction is m^{th} order with respect to A, n^{th} order with respect to B, and the overall order is m+n.** (1P)

(i) Give the equation that describes the influence of temperature on the rate of a chemical reaction. (1P)
$k(T) = A\cdot\exp(-E_{act}/RT)$

(j) Determine the stoichiometric coefficients for the substances in the following redox reactions, and give their oxidation numbers:

[**3**] Fe + [**2**] NO_3^- + [**8**] H^+ → [**3**] Fe^{2+} + [**2**] NO + [**4**] H_2O
Fe: 0 N: +5 Fe: +2 N: +2 (2P)

[**5**] $NaNO_2$ + [**2**] $KMnO_4$ + [**3**] H_2SO_4 → [**5**] $NaNO_3$ + [**2**] $MnSO_4$ + [**1**] K_2SO_4 + [**3**] H_2O
N: +3 Mn: +7 N: +5 Mn:+2 (2P)

[**1**] MnO_2 + [**4**] HBr → [**1**] $MnBr_2$ + [**1**] Br_2 + [**2**] H_2O
Mn: +4 Br: -1 Mn: +2 Br: 0 (2P)

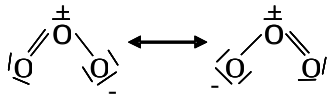
Calculate the potential E_{cell} of a Galvanic cell in which a Zn electrode is immersed in a 1 molar solution of $ZnSO_4$, and a Cu electrode is immersed in a 1 molar solution of $CuSO_4$? What are the redox half-reactions at each electrode? (3P)

Anode: $Zn \rightarrow Zn^{2+} + 2\ e^-$
Kathode: $Cu^{2+} + 2\ e^- \rightarrow Cu$
E = +0.76 -(-0.34) V = +1.10 V

Question 3:

a) Give the equation for the acid-base reaction between ethanoic acid and ammonia. How are acids and bases defined according to the theory of Lowry and Brønsted?
$NH_3 + HOOCCH_3 \rightarrow NH_4^+ + {}^-OOCCH_3$
Acid: Proton donor; Base: Proton acceptor (2P)

b) Draw the Lewis structure for the ozone (O_3) molecule, and give the chemical equation for the formation of ozone (2P)



$O_2(g) \rightarrow 2O(g)$ (high T or UV irradiation)
$O(g) + O_2(g) \rightarrow O_3(g)$

c) What are the oxidation numbers of the nitrogen atoms in N_2O, N_2, NH_3 and NO_2? (2P)

N_2O: 1; N_2: 0; NH_3: -3; NO_2: +4

d) Give one property of iron that is important in the industrial use of the metal.

High melting point, high tensile strength, ductility, magnetisation (1P)

e) Name two raw materials from which iron can be obtained (1P)

Two from Magnetite (Fe_3O_4), Haematite (Fe_2O_3), Limonite ($Fe_2O_3 \cdot nH_2O$ or "$FeO(OH) \cdot nH_2O$"), Siderite ($FeCO_3$), Pyrites (FeS_2)

f) What is the reducing agent in a Blast Furnace? Give the equation for the reaction in which Fe is formed in a Blast Furnace. (The equation for the overall reaction of a raw material to give metallic Fe is sufficient). (2P)
***Reducing agent:* CO**
$FeO + CO \rightarrow Fe + CO_2$
or $Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$
or $Fe_3O_4 + 4\ CO \rightarrow 3\ FeO + 4\ CO_2$

g) In a Blast Furnace, finely-divided carbon is formed via the Boudouard equilibrium and dissolves into the newly-formed iron. Give the equation for the Boudouard equilibrium.
$CO_2 + C \leftrightarrows 2\ CO$ (1P)

What negative effect does this dissolved carbon have on the properties of Pig Iron?
The pig iron is brittle (1P)
Give the name of a process from steel production, by which this carbon content can be reduced
Air-refining (1P)

h) The reduction of copper ores results in impure copper metal. What method is used to convert this crude product into high-purity copper? Give the equations for the reactions that take place. What solid substances are obtained from this process in addition to the pure copper? (3P)
Electrolysis with an anode of raw copper and a cathode of pure copper
Anode: $Cu \rightarrow Cu^{2+} + 2\ e^-$

Cathode: $Cu^{2+} + 2\ e^- \rightarrow Cu$
Solid "anode sludge" containing Ag, Au etc

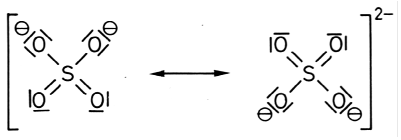
i) Give the equations for the reactions that take place when iron rusts in damp air. (2P)

$Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$
$O_2(g) + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-(aq)$
$Fe^{2+}(aq) + 2\ OH^-(aq) \rightarrow Fe(OH)_2(s)$
Then $2\ Fe(OH)_2(s) + 1/2\ O_2 \rightarrow Fe_2O_3(s) + H_2O$

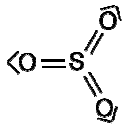
j) Name two important methods that can prevent the rusting of iron described in question (i) above (2P)

Coatings (paint, plastic, enamel)
Sacrificial electrodes (Mg or Zn)
Passivation (either natural: Zn, Al, or through addition of e.g. Cr)
Electroplating or galvanisation

k) Draw the Lewis structures for SO_3 and the sulphate anion $(SO_4)^{2-}$. What are the oxidation states of S and O in each case? (4P)

SO_4^{2-}: 

S: +6, O: -2

SO_3: 

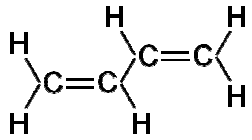
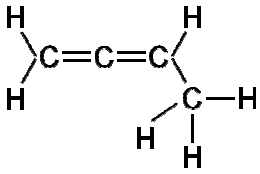
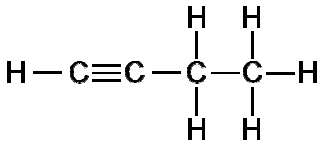
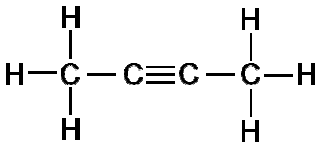
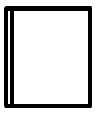
S: +6, O: -2

l) Name two modifications (allotropes) of carbon and describe the structure of each (2P)

Graphite: Layer structure, stacked "graphene" sheets each made up of fused hexagons of sp^2-hybridised C atoms.
Diamond: 3-D structure, in which each sp^3-hybridised C atom forms single bonds to four other tetrahedrally-arranged C atoms
Fullerenes: cage-like molecules with sp^2-hybridised C atoms forming fused hexagons and pentagons.
Nanotubes: tube-like structures formed by "rolling up" a graphehe sheet.
Any two of these – sketches are often helpful!

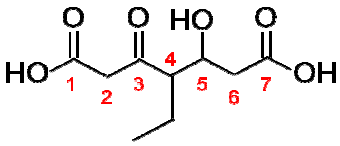
Question 4:

a) There are five organic compounds with the sum formula C_4H_6. Choose any <u>two</u> of these, and draw their Lewis formulae, give their correct names, and state which class of organic compound each of them belongs to. (3P)

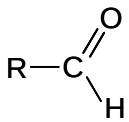
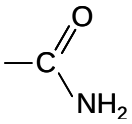
	
Alkene	**Alkene (or allene)**
Buta-1,3-diene	**Buta-1,2-diene**
	
Alkyne	**Alkyne**
1-Butyne	**2-Butyne**
	
Cycloalkene	
Cyclobutene	

½P each for Lewis formula, class and correct name

b) Give the Lewis structure for the molecule 4-ethyl-5-hydroxy-hept-3-one-1,7-dicarboxylic acid (4P)

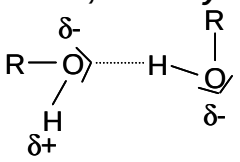


c) Give the Lewis structures of the characteristic functional groups of ethers, aldehydes and primary amides (3P)

R-O-R‘	Ethers
	Aldehydes
	Primary amides

d) Explain why an alcohol has a much higher boiling point than the corresponding alkane with the same number of carbon atoms. Why is ethane hydrophobic, whereas ethanol is hydrophilic? (2P)

Higher boiling point: -OH groups of alcohol form intermolecular hydrogen bonds, but only much weaker Van der Waals forces between alkane molecules



Ethanol molecules can form H-bonds to surrounding water molecules; ethane cannot.

Give the equation and the reaction conditions for the industrial synthesis of methanol. Give the reaction equation for the synthesis of ethanoic acid from methanol (2P)

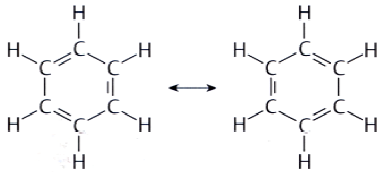
Synthesis: $CO + 2\,H_2 \xrightarrow{380°C;\, p > 200\,bar} CH_3OH$ **(Gl. 1P, Wärme, Druck: 1P)**

Give the reaction equation for the synthesis of ethanoic acid from methanol.

$CH_3OH + CO \rightarrow CH_3COOH$ (1P)

e) Give three structural characteristics of the benzene molecule, and draw the Lewis-structures of the two mesomeric structures. (3P)

3 from: planar hexagon of C atoms, all C-C bonds equal length, bond angles 120º, 6 delocalised π-molecular orbitals, C atoms sp^2 hybridised.



f) Describe with the help of reaction equations the radical chlorination of ethane to chloroethane.

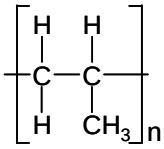
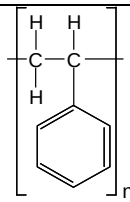
$Br_2 \rightarrow Br\cdot + \cdot Br$ **Initiation** (1P)

$H_3C\text{-}CH_3 + \cdot Br \rightarrow H_3C\text{-}CH_2\cdot + HBr$
$H_3C\text{-}CH_2\cdot + Br_2 \rightarrow H_3C\text{-}CH_2Br + \cdot Br$ **Propagation reactions** (1P)

$Br\cdot + \cdot Br \rightarrow Br_2$
$R-CH_2\cdot + \cdot Br \rightarrow R-CH_2Br$
$R-CH_2\cdot + R-CH_2\cdot \rightarrow R-CH_2\text{-}CH_2-R$ **Termination** (1P)

g) What are the two principal types of mechanisms for polymerisation reactions?
Radical reactions and condensation reactions (1P)

h) Give the structures of the repeating units in polypropene, polystyrene und polyvinylchloride (3P)

Polypro-pene		Polystyrene		Polyvinyl-chloride